



Preparation and characterization of sulfonated poly(ether ether ketone)/poly(vinylidene fluoride) blend membrane for vanadium redox flow battery application

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HIGHLIGHTS

- SPEEK/PVdF (S/P) blend membranes are first employed in vanadium redox flow battery.
- S/P blend membranes are dense and uniform accompanied with high ion selectivity.
- High VRB single cell efficiencies are obtained by using S/P blend membranes.
- VRB with S/P 15 shows stable cycling performances and slow capacity decline.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 28 January 2013

Received in revised form

25 February 2013

Accepted 2 March 2013

Available online 14 March 2013

Keywords:

Vanadium redox flow battery

Sulfonated poly(ether ether ketone)

Poly(vinylidene fluoride)

Blend membrane

Ion selectivity

ABSTRACT

Blend membranes of sulfonated poly(ether ether ketone) (SPEEK) and poly(vinylidene fluoride) (PVdF) are prepared with various mixing mass ratios for vanadium redox flow battery application for the first time. The SPEEK/PVdF blend membranes are characterized by scanning electron microscopy and energy dispersive X-ray spectroscopy. The water uptake, swelling ratio, ion exchange capacity, proton conductivity, VO^{2+} permeability, ion selectivity, single cell performance and mechanical property of blend membranes are detailed evaluated. The blend membranes are dense and uniform when PVdF mass ratio ranges from 5 wt.% to 20 wt.%. The blend membrane with 15 wt.% PVdF (denoted as S/P 15) is further investigated for its good balance of proton conductivity and ion selectivity. The cell with S/P 15 membrane shows higher coulombic efficiency and energy efficiency compared with Nafion 117 membrane (98.0% vs. 92.0% and 81.0% vs. 75.8%, respectively). Furthermore, no obvious efficiency declines are observed after 80 cycles cell test accompanied with a lower discharge capacity decay rate.

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1. Introduction

Vanadium redox flow battery (VRB), which was proposed in 1985 and developed by Skyras-Kazacos et al., has been well

accepted as a superior large-scale energy storage system in the past decades for its advantages of high energy efficiency, long cycle life, fast response time, low operation cost and flexible, modular design [1–3]. It employs $\text{V}^{2+}/\text{V}^{3+}$ and $\text{VO}^{2+}/\text{VO}_2^+$ redox couple as the

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negative and positive electrolytes respectively, porous carbon fabric materials as electrodes, and proton exchange membranes (PEMs) as the anolyte/catholyte separators. Various research progresses of high activity electrodes, high stability and concentration electrolytes have been reported [4–9], which are improving the performance of VRB. However, lack of low cost membranes with low vanadium ion permeability and long cycle life is limiting the commercial application of VRB [10]. An ideal PEM should possess advantages such as high proton conductivity, low vanadium ion permeability, good chemical stability, and low cost, which are recognized in recent years [11].

Nafion membrane, one of the perfluorosulfonic polymer, is widely used as the benchmark PEM in VRB system due to its high proton conductivity and excellent chemical stability. However, Nafion membrane has a relatively high vanadium ion permeability which leads to lower coulombic efficiency, lower energy efficiency, and faster capacity decline [12,13]. Various Nafion composite or layered membranes have been prepared by different modification methods, which decrease the vanadium ion permeability while maintain the proton conductivity at a relatively high level. Modified membranes which exhibit better performances than pristine Nafion membrane include organic–inorganic hybrid membranes of Nafion and SiO₂ [14–16] or TiO₂ [17,18], organic–organic composite membranes of Nafion and polytetrafluoroethylene [19] or sulfonated poly(arylene ether)s [20]. However, the modified membranes are still too expensive for large-scale VRB system. Therefore, it is urgent to develop alternative low cost membranes to reduce the capital cost of VRB system.

Sulfonated poly aromatic membranes including sulfonated poly(arylene ether)s [21], sulfonated poly(arylene ether ketone)s [22–24], sulfonated poly(arylene sulfone)s [25], and sulfonated poly(arylene ether sulfone)s [26] were prepared and used as new PEMs in VRB. In these membranes, sulfonated poly(ether ether ketone) (SPEEK) is paid more attention for its high performance and easy preparation. However, the high swelling ratio possessed by SPEEK membrane with a high degree of sulfonation would result in lower mechanical property and higher vanadium ion permeability, which are limiting its further application in VRB. Blending SPEEK with other polymer is regarded as an effective method to avoid the problems mentioned above. Poly(vinylidene fluoride) (PVdF), a hydrophobic polymer with high crystallinity, high mechanical property and good chemical stability, is regarded as a promising choice to blend with high degree of sulfonation SPEEK. The SPEEK/PVdF blend membrane was prepared and utilized in proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) [27–29], which successfully decreased the swelling ratio and permeability of blend membrane compared with pristine SPEEK membrane.

Inspired by the good performances of SPEEK/PVdF blend membranes in PEMFCs and DMFCs, in this work, SPEEK/PVdF blend

membranes with various mixing mass ratios were prepared by solution casting method, characterized, and utilized in VRB for the first time. The physicochemical properties and morphologies of membranes accompanied with their performances in VRB single cell test were detailed investigated.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (PEEK) (Victrex, PEEK 450P) was washed and then dried at 100 °C for 24 h in vacuum. Poly(vinylidene fluoride) (PVdF)($M_w = 900000$, powder) was purchased from Shanghai 3F New Material Co., Ltd., China. Nafion 117 membrane was purchased from Dupont company. All the other analytical reagents, including *N,N*-Dimethylformamide (DMF), H₂SO₄, NaCl, NaOH, MgSO₄·7H₂O and VOSO₄·4H₂O, were purchased from common commercial suppliers and used without further purification.

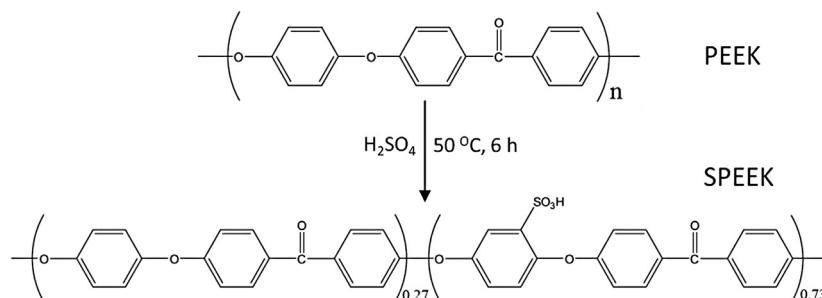
2.2. Preparation of sulfonated PEEK

Scheme 1 shows the sulfonation reaction of PEEK. SPEEK was prepared by following modified procedures as previous article reported [30]. PEEK was dried at 80 °C for 6 h in vacuum before using. 25 g PEEK was slowly added into 250 mL H₂SO₄ (95–98 wt.%) to form a 10 wt./vol.% reaction solution, and the solution was vigorously stirred at 50 °C in water bath for 6 h. The sulfonation reaction was terminated by slowly pouring the polymer solution into large amount of ice-cold deionized water under vigorous mechanical agitation. The polymer was washed several times with deionized water until the pH of water was 7 and then was filtered. The SPEEK polymer was dried at 60 °C for 24 h, then dried at 100 °C for 24 h in vacuum.

2.3. Membrane preparation

SPEEK membrane was prepared by following procedures. 1.5 g SPEEK was dissolved in 10 mL DMF and magnetic stirred for 24 h to form a 15 wt./vol.% casting solution. The casting solution was cast on a flat, clean plate glass, controlled at a fixed thickness, dried at 60 °C for 24 h, and then dried at 100 °C for 24 h in vacuum. The SPEEK membrane was peeled off from the plate glass by immersing in deionized water and then immersed in 1 mol L^{−1} H₂SO₄ solution for 24 h. After acidification, the SPEEK membrane was immersed in deionized water for 48 h to remove excess H₂SO₄ solution. The SPEEK membrane was stored in deionized water at room temperature before test.

The SPEEK/PVdF blend membranes with 5, 10, 15, 20 and 30 wt.% PVdF were prepared by following procedures. Maintaining the total weight of SPEEK and PVdF at 1.5 g, desired weight of PVdF was



Scheme 1. Preparation of SPEEK (DS = 0.73 in this work).

dissolved in 10 mL DMF and magnetic stirred for 12 h. Then the rest weight of SPEEK was slowly added into the PVdF solution and magnetic stirred for 24 h to form a homogeneous solution. The homogeneous solution was cast on a plate glass, controlled at a fixed thickness, dried at 60 °C for 24 h, and then dried at 100 °C for 24 h in vacuum. The SPEEK/PVdF blend membranes were peeled off from plate glass, immersed in 1 mol L⁻¹ H₂SO₄ solution for 24 h, immersed in deionized water for 48 h, and stored in deionized water at room temperature before test. The blend membranes are denoted as S/P X, where X is the PVdF mass ratio. For example, S/P 15 is a blend membrane with 15 wt.% PVdF and 85 wt.% SPEEK. The thicknesses of wet SPEEK and S/P blend membranes are controlled between 70 and 85 μm.

As a comparison, Nafion 117 membrane was treated by the standard procedures as previous article reported [19]. The Nafion 117 membrane was immersed in 3 wt.% H₂O₂ solution, deionized water, 1 mol L⁻¹ H₂SO₄ solution and deionized water in order, with the same treatment condition of 80 °C for 1 h. The thickness of wet Nafion 117 membranes is 215 μm.

2.4. Membrane characterization

2.4.1. Water uptake and swelling ratio

Water uptake of membrane was determined in H⁺ form and conducted by following procedures. The sample membrane was immersed in deionized water for 24 h at room temperature. The wet weight (W_{wet}) of sample membrane was measured after quickly wiping off the excess water on the surface of the sample membrane with filter papers. Then the sample membrane was dried at 100 °C for 24 h in vacuum. The dry weight (W_{dry}) of sample membrane was measured after the temperature of sample membrane getting to room temperature in vacuum. The water uptake of membrane was calculated by following equation:

$$\text{Water uptake}(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

To obtain the swelling ratio of membrane, the rectangle sample membrane was immersed in deionized water at room temperature for 24 h. The wet length (l_{wet}) of sample membrane was measured after wiping off the excess water on the surface of the sample membrane. Then the sample membrane was dried at 100 °C for 24 h in vacuum, and then the dry length (l_{dry}) of sample membrane was measured. The swelling ratio was calculated by following equation:

$$\text{Swelling ratio}(\%) = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \times 100\% \quad (2)$$

2.4.2. Ion exchange capacity (IEC) and proton conductivity

The ion exchange capacity (IEC) was measured by traditional titration method. The sample membrane with a known dry weight was firstly immersed in deionized water at room temperature for 24 h, then immersed in 50 mL saturated NaCl solution for 24 h to turn the membrane into Na⁺ form. The resulting solution was titrated with 0.1 mol L⁻¹ NaOH solution using phenolphthalein pH indicator to indicate the finishing point. The IEC was calculated by following equation:

$$\text{IEC}\left(\text{mmol g}^{-1}\right) = \frac{C_{\text{NaOH}} \times V_{\text{NaOH}}}{W_{\text{dry}}} \quad (3)$$

where IEC is the ion exchange capacity (mmol g⁻¹), C_{NaOH} is the concentration of the NaOH solution (mol L⁻¹), V_{NaOH} is the volume

of the consumed NaOH solution (mL), and W_{dry} is the dry weight of the sample membrane (g).

The degree of sulfonation (DS) of pristine SPEEK membrane was calculated by following equation:

$$\text{DS}(\%) = \frac{288 \times \text{IEC}}{1000 - 80 \times \text{IEC}} \times 100\% \quad (4)$$

where DS is the degree of sulfonation of pristine SPEEK membrane, IEC is the ion exchange capacity (mmol g⁻¹) of pristine SPEEK membrane, 288 is the monomer molar mass (g mol⁻¹) of PEEK, 80 is the increase of monomer molar mass (g mol⁻¹) after one —SO₃H group replacing one —H group, and 1000 is the calculation factor when the other value units are the same as mentioned above.

The proton conductivity of sample membrane was measured by electrochemical impedance spectroscopy (EIS) using a PARSTAT 2273 electrochemical station (USA, AMETEK, Inc.) as previous article reported [11]. The sample membrane was firstly immersed in deionized water at room temperature for 24 h, and then was tested. The measurement was conducted between frequencies of 1 MHz and 1 Hz with amplitude of 10 mV. The proton conductivity (σ) was calculated by following equation:

$$\sigma\left(\text{mS cm}^{-1}\right) = \frac{L}{A \times R} \quad (5)$$

where σ is the proton conductivity of sample membrane, L is the thickness and A is the effective area of sample membrane after immersing in deionized water for 24 h, and R is the intercept of high frequency complex impedance with the RE (Z') axis.

2.4.3. VO²⁺ permeability and ion selectivity

The VO²⁺ permeability was measured by using a membrane separated diffusion cell as previous article reported [15]. The sample membrane (effective area 7 cm²) was firstly located between two reservoirs, then the left reservoir was filled with 40 mL 1.5 mol L⁻¹ VOSO₄ in 3 mol L⁻¹ H₂SO₄ solution and the right reservoir was filled with 40 mL 1.5 mol L⁻¹ MgSO₄ in 3 mol L⁻¹ H₂SO₄ solution, respectively. The two solutions were magnetic stirred at room temperature throughout the measurement. 3 mL MgSO₄ solution of right reservoir was taken out at a regular time interval, and the VO²⁺ concentration was measured with a Spectrum lab 752S UV–Vis spectrophotometer (China, Leng Guang Tech.). The 3 mL taken out MgSO₄ solution was put back into the right reservoir after each measurement. The VO²⁺ permeability was calculated by following equation:

$$V_R \frac{dC_R(t)}{dt} = \frac{A \times P}{L} (C_L - C_R(t)) \quad (6)$$

where V_R is the volume of MgSO₄ solution, C_R is the VO²⁺ concentration in the MgSO₄ solution, t is time, A is the effective area of sample membrane, L is the thickness of sample membrane, P is the VO²⁺ permeability, and C_L is the VO²⁺ concentration in the left reservoir. During the whole measurement, the changes of C_L and $C_R(t)$ were small and negligible, so the $(C_L - C_R(t))$ was almost constant equaled with the beginning VO²⁺ concentration of left reservoir. Then the VO²⁺ permeability (P) could be easily calculated.

The ion selectivity of membrane (S) was defined as proton conductivity (σ) dividing VO²⁺ permeability (P), which can be calculated by following equation:

$$S = \frac{\sigma}{P} \quad (7)$$

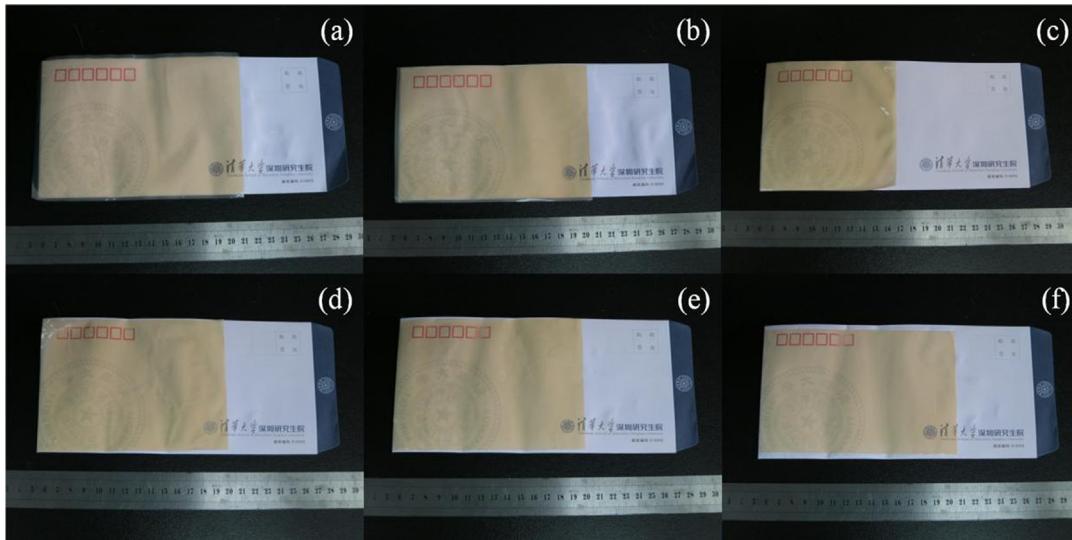


Fig. 1. Photographs of membranes: (a) SPEEK; (b) S/P 5; (c) S/P 10; (d) S/P 15; (e) S/P 20; (f) S/P 30.

2.4.4. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

Both the morphology and EDX of the membranes cross-sections were observed by SEM (Hitachi S-4800, Japan). The morphology of SPEEK and S/P blend membranes was examined, while only the EDX of S/P 15 and S/P 30 membranes was conducted. The gold sputter coating was conducted on the desired sample membranes before test.

2.4.5. Mechanical property

The mechanical property of membrane was evaluated with a computer-controlled universal testing machine (CMT5504, Suns Aspect Technology Co., Ltd., China). The sample membrane with $70\text{ mm} \times 10\text{ mm}$ dimensions was cut and used for mechanical property test. The gauge length and tensile speed were 30 mm and 2 mm min^{-1} , respectively. Breaking strength, percentage elongation and elastic modulus of membranes were identified.

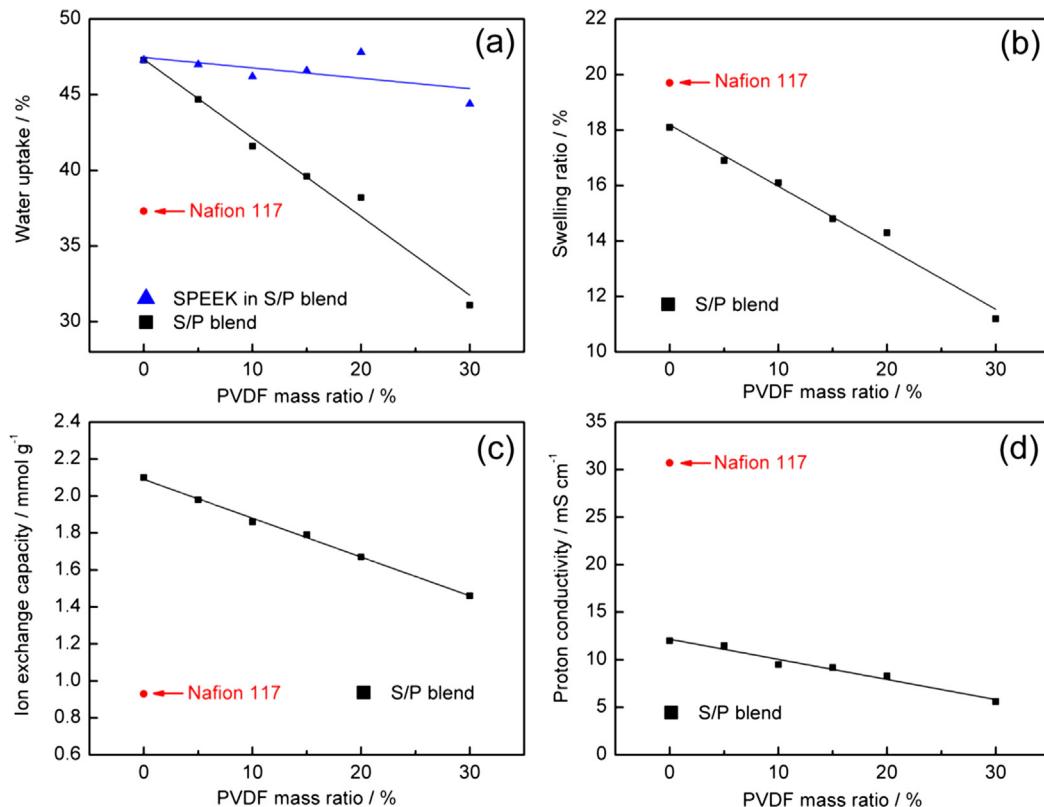


Fig. 2. Physicochemical properties of Nafion 117, SPEEK and S/P blend membranes.

2.5. VRB single cell performance

The VRB single cell used for charge–discharge test was fabricated by sandwiching a membrane (70 mm × 70 mm) between two pieces of graphite felts (50 mm × 50 mm × 5 mm, Gansu Haoshi Carbon Fiber Co., Ltd., China) served as electrodes and two pieces of graphite polar plates (60 mm × 60 mm × 3 mm, Shanghai Hongfeng Industrial Co., Ltd., China) served as current collectors. All these components were fixed between two thick flat plastic plates with stainless screws. Two 60 mL solutions of 2 mol L⁻¹ VO²⁺/V³⁺ (mol:mol = 1:1) in 2 mol L⁻¹ H₂SO₄, which were served as negative and positive starting electrolytes respectively, were cyclically pumped into the corresponding half cell by two peristaltic pumps (BT00-300T, Longer Pump Co., Ltd., China) with a revolution speed of 40 rpm (a flow rate of 60 mL min⁻¹). The VRB single cell was charged and discharged by a battery testing system (CT-3008W-5V6A-S1-F, Neware Electronics Co., Ltd., China).

The VRB single cell was charged and discharged at current densities of 40, 50, 60, 70 and 80 mA cm⁻² to get charge–discharge performance of different membranes. To avoid the corrosion of graphite felt electrodes and graphite polar plates, the charge–discharge voltages were limited between 1.65 V and 0.8 V, respectively. The self-discharge test was conducted to investigate the transfer of vanadium ions across membranes under actual condition. The VRB single cell was charged to 50% state of charge (1600 mAh of capacity) with the constant current density of 40 mA cm⁻² and then the self-discharge test began. The test was stopped when the open circuit voltage (OCV) was lower than 0.8 V. The cycle life test was conducted at the constant current density of 60 mA cm⁻² and the charge–discharge voltages were limited between 1.65 V and 0.8 V, respectively. The coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) were calculated by following equations:

$$\text{CE}(\%) = \frac{\int I_d dt}{\int I_c dt} \times 100\% \quad (8)$$

$$\text{EE}(\%) = \frac{\int V_d I_d dt}{\int V_c I_c dt} \times 100\% \quad (9)$$

$$\text{CE}(\%) = \frac{\text{EE}}{\text{VE}} \times 100\% \quad (10)$$

where I_d is the discharging current, I_c is the charging current, V_d is the discharging voltage, and V_c is the charging voltage.

Table 1
Physicochemical properties data of Nafion 117, SPEEK and S/P blend membranes.

Membrane	Thickness (μm, wet)	Water uptake (%)	Swelling ratio (%)	IEC (mmol g ⁻¹)	Proton conductivity (mS cm ⁻¹)
Nafion 117	215	37.3	19.7	0.93	30.7
SPEEK	79	47.3	18.1	2.10	12.0
S/P 5	84	44.7 ^a /47.0 ^b	16.9	1.98	11.5
S/P 10	75	41.6 ^a /46.6 ^b	16.1	1.86	9.5
S/P 15	74	39.6 ^a /46.6 ^b	14.8	1.79	9.2
S/P 20	72	38.2 ^a /47.8 ^b	14.3	1.67	8.3
S/P 30	70	31.1 ^a /44.4 ^b	11.2	1.46	5.6

^a The calculation of water uptake is based on the weight of the entire sample membrane.

^b The calculation of water uptake is based on the weight of SPEEK content in sample membrane.

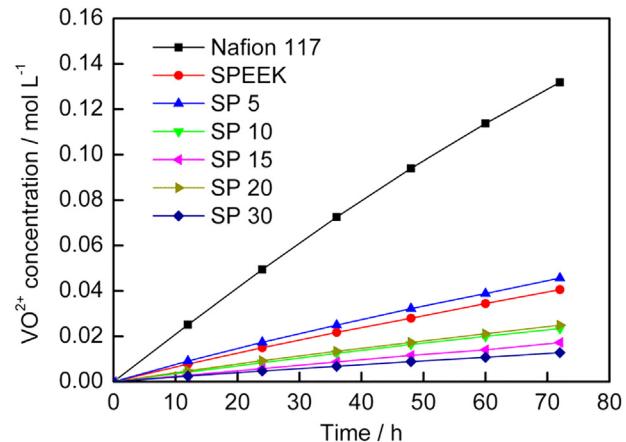


Fig. 3. Change of VO²⁺ concentrations in MgSO₄ solutions with time for Nafion 117, SPEEK and S/P blend membranes.

3. Results and discussion

3.1. Photographs and physicochemical properties

Fig. 1 shows the digital images of the membranes prepared by solution casting method. It can be seen that the membranes are pale yellow colors and homogeneous with no pinholes. Furthermore, all the envelopes behind the membranes can be visibly seen, which indicates that all the membranes possess certain transparencies.

Fig. 2 represents the water uptake, swelling ratio, IEC and proton conductivity of Nafion 117, SPEEK and S/P blend membranes with various PVdF mass ratios, and the data of these physicochemical properties are listed in Table 1. It can be observed that the water uptake of blend membranes decreases with the increasing of PVdF mass ratio (the black line in Fig. 2a). The water uptake values of most blend membranes are higher than Nafion 117 membrane. High water uptake is good for IEC and proton conductivity, because the increasing of water uptake would facilitate the dissociation of –SO₃H groups and the migration of protons in the membrane [31]. However, when the calculation of water uptake is based on the weight of SPEEK content in the blend membranes, the water uptake values of blend membrane are between 44% and 48% (the blue line in Fig. 2a), which is close to the value of pristine SPEEK (47%). These results indicate that the water adsorption of blend membranes is

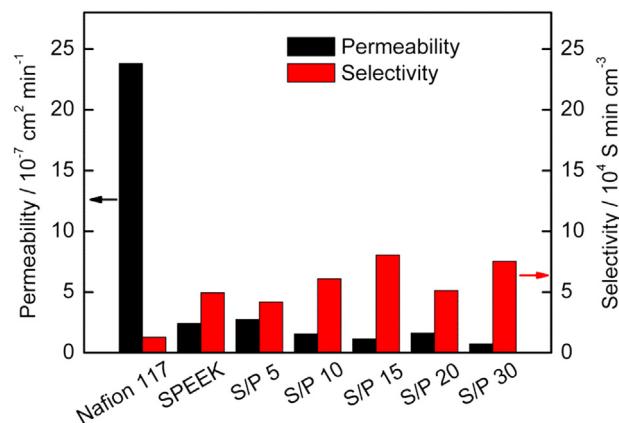


Fig. 4. VO²⁺ permeability and ion selectivity of Nafion 117, SPEEK and S/P blend membranes.

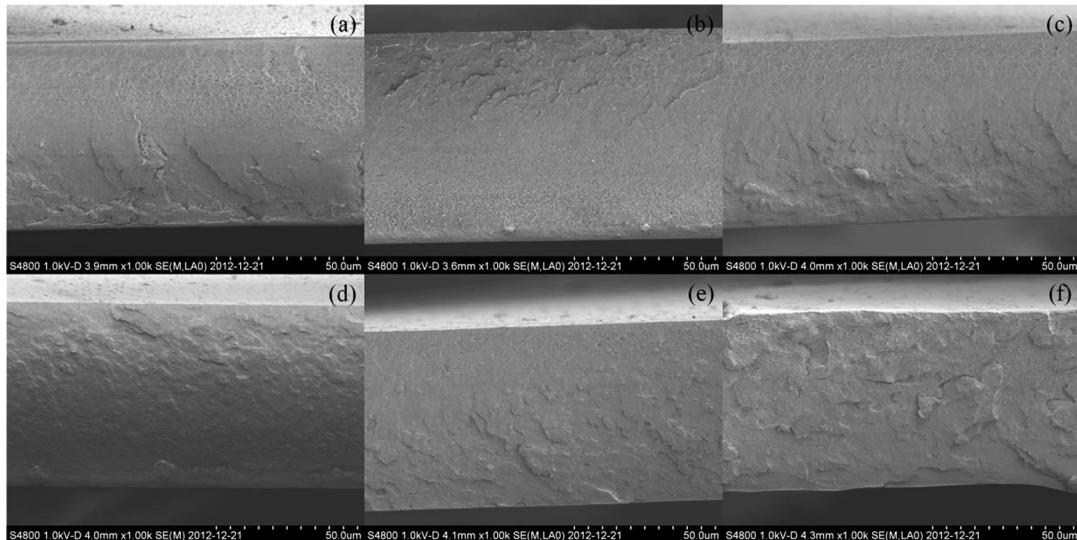


Fig. 5. SEM images of membranes cross-sections: (a) SPEEK; (b) S/P 5; (c) S/P 10; (d) S/P 15; (e) S/P 20 and (f) S/P 30.

almost generated by the SPEEK content while the addition of PVdF has no effect in suppressing the water adsorption, which is opposite to the previous report [31].

The swelling ratio of SPEEK and S/P blend membranes is illustrated in Fig. 2b. The swelling ratio of blend membranes decreases with the increasing of PVdF mass ratio, which indicates that the swelling behaviors of blend membranes are indeed suppressed by PVdF because of the extending of crystalline region in the blend membranes. Furthermore, the swelling ratio of blend membranes decreases with a larger extent compared with the decrease extent of SPEEK, which means that there is interaction between SPEEK and PVdF in the swelling behavior.

The IEC of various membranes is shown in Fig. 2c. The IEC of blend membranes monotonically decreases with the increasing

PVdF mass ratio, which is owing to the decrease of $-\text{SO}_3\text{H}$ groups contributing to the IEC. The IEC and PVdF mass ratio is a linear relationship ($R^2 = 0.996$), which means that there is practically no interaction between SPEEK and PVdF in this measurement. The degree of sulfonation (DS) of pristine SPEEK membrane is 0.73, which can be calculated from the IEC value (2.10 mmol g^{-1}) according to the equation (4).

The proton conductivity of various membranes is presented in Fig. 2d. It can be seen that the proton conductivity of blend membranes decreases with the increasing PVdF mass ratio. The proton conductivity is dependent on chemical structure, morphology, IEC, water uptake and temperature, especially the water uptake and IEC [31]. As discussed above, the water uptake and IEC decrease with the increasing of PVdF mass ratio, therefore the proton conductivity

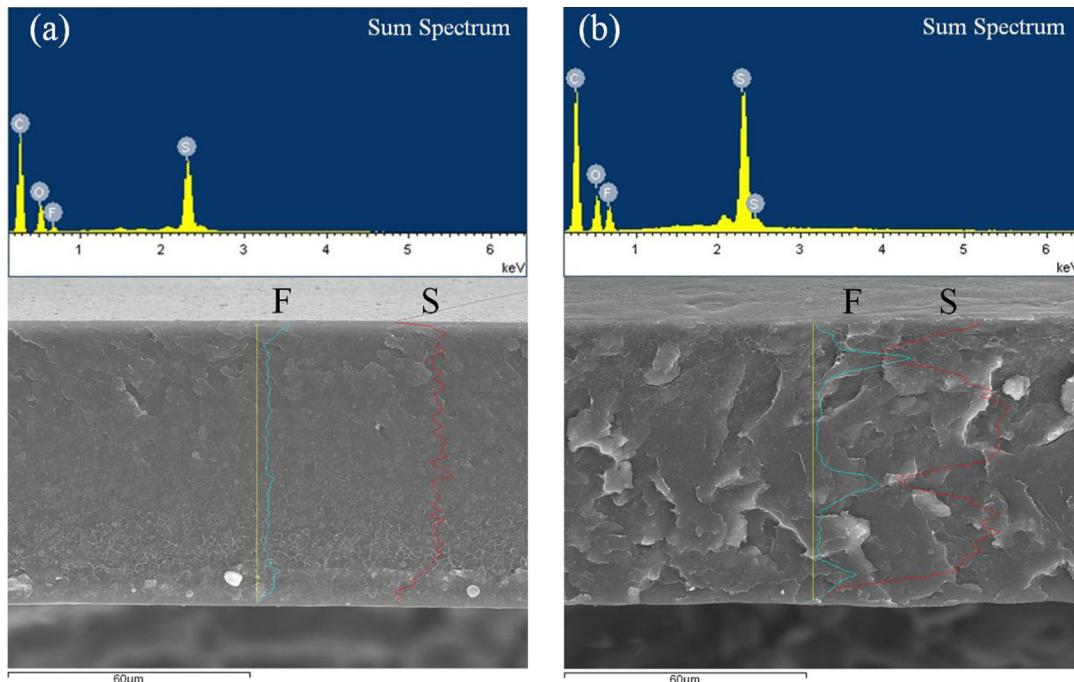


Fig. 6. EDX images of membranes cross-sections: (a) S/P 15 and (b) S/P 30.

trend of blend membranes could be expected. Although the proton conductivity values of blend membranes (for example, S/P 15 membrane is 9.2 mS cm^{-1}) are lower than Nafion 117 membrane (30.7 mS cm^{-1}), the blend membranes still possess effective VRB cell performances, which could be verified by following results.

3.2. VO^{2+} permeability and ion selectivity

The change of VO^{2+} concentrations in MgSO_4 solutions with time for various membranes is illustrated in Fig. 3. All the VO^{2+} concentrations of various membranes change linearly with time, and the VO^{2+} ion diffusion speed across blend membranes is slower than Nafion 117 membrane. The VO^{2+} permeability is calculated and shown in Fig. 4. The VO^{2+} permeability values of blend membranes (between 0.74 and $2.75 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$) are smaller than Nafion 117 membrane ($23.84 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$). The different VO^{2+} permeability of these membranes can be explained by the differences of microstructures [32]. In general, the backbone of SPEEK membrane is less hydrophobic and the $-\text{SO}_3\text{H}$ group is less acidic, which results in smaller hydrophilic/hydrophobic separation accompanied with higher dispersed $-\text{SO}_3\text{H}$ groups. Furthermore, the less softness of SPEEK backbone also prevents the neighboring dispersed $-\text{SO}_3\text{H}$ groups to form bigger clusters. Thus the water filled channels in SPEEK membrane are narrow and branched with more dead end pockets compared with Nafion membranes. The migration of vanadium ion in these membranes is therefore slower than Nafion membranes.

The proton conductivity (σ) and vanadium ion permeability (P) are usually found having an antagonistic relationship, which is attracting more attentions in recent years [21]. Therefore, the ion selectivity (S , defined as σ/P) becomes an important parameter in membrane design while keeping the balance of proton conductivity and ion permeability. The ion selectivity of various membranes is also calculated and shown in Fig. 4. It can be seen that all the ion selectivity values of S/P blend membranes are higher than Nafion 117 membrane ($1.29 \times 10^5 \text{ S min cm}^{-3}$), especially S/P 15 membrane ($8.06 \times 10^5 \text{ S min cm}^{-3}$) and S/P 30 membrane ($7.53 \times 10^5 \text{ S min cm}^{-3}$), which is due to the lower permeability values of S/P blend membranes compared with Nafion 117 membrane. Thus, the SPEEK, S/P 15 and S/P 30 membranes are chosen to further investigate.

3.3. SEM and EDX

The morphology of the blend membranes cross-sections is examined by SEM and the resulting images are illustrated in Fig. 5. As shown in Fig. 5, when PVdF mass ratio ranges from 5 wt.% to 20 wt.%, the blend membranes are dense and uniform with no visible hole, which indicates that the blend membranes are homogeneous. The EDX of S/P 15 and S/P 30 membranes cross-sections is further investigated and shown in Fig. 6. The signal element F for the presence of PVdF and the signal element S for the presence of $-\text{SO}_3\text{H}$ group from SPEEK are uniformly distributed in the S/P 15 membrane with few differences near the surface of membrane (Fig. 6a), which reveals that the S/P 15 membrane has a homogeneous microstructure. However, the F element and S element are non-uniformly distributed in the S/P 30 membrane, which reveals that the S/P 30 membrane is heterogeneous with a phase-separated microstructure.

3.4. VRB single cell performance

Nafion 117, SPEEK, S/P 15 and S/P 30 membranes are chosen to conduct the VRB single cell test. The single cycle charge-discharge curves of these membranes at 60 mA cm^{-2} are illustrated in Fig. 7.

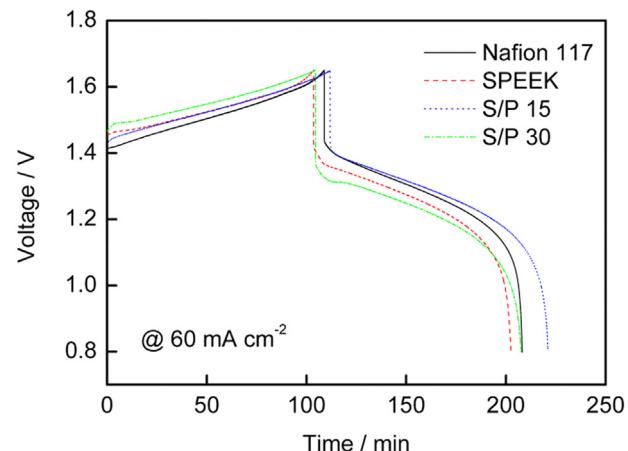


Fig. 7. Charge-discharge curves of VRBs with Nafion 117, SPEEK, S/P 15 and S/P 30 membranes at 60 mA cm^{-2} .

Low membrane resistance and vanadium ion permeability could help to improve the charge and discharge capacity, which could be replaced by the high proton conductivity and ion selectivity in this work. It can be seen that the S/P 15 membrane has the highest charge and discharge capacity among these membranes, which can be due to its good balance of proton conductivity and ion selectivity. Furthermore, the lower charge capacity of S/P 30 membrane compared with Nafion 117 membrane could be caused by the lower proton conductivity (higher membrane resistance), and the higher discharge capacity can be assigned to the higher ion selectivity (lower vanadium ion permeability) of S/P 30 membrane.

Open circuit voltage (OCV) of VRB with various membranes is illustrated in Fig. 8. It can be seen that the OCV decay rates of S/P 15 and S/P 30 membranes are lower than Nafion 117 membrane. The self-discharge time of Nafion 117, SPEEK, S/P 15 and S/P 30 membranes is 68 h, 111 h, 118 h and 240 h respectively, which is agreeing well with the VO^{2+} permeability results.

Fig. 9 shows the coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) of VRBs with various membranes in different current densities. The rank of CE is S/P 30, S/P 15, SPEEK and Nafion 117 membranes at all current densities, which is also agreeing well with the VO^{2+} permeability results. The highest EE is VRB with S/P 15 membrane, which is due to its highest ion

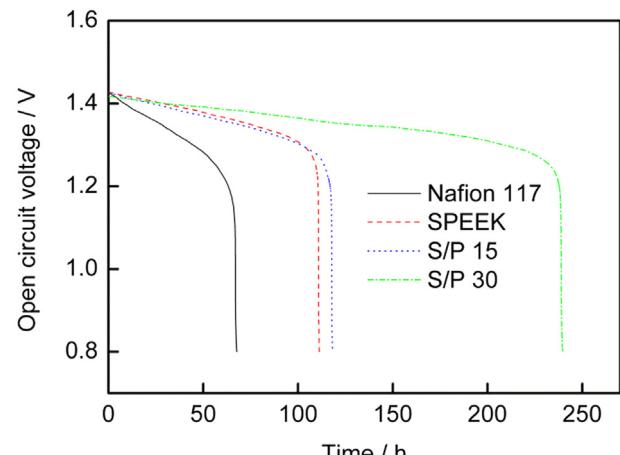


Fig. 8. Open circuit voltage curves of VRBs with Nafion 117, SPEEK, S/P 15 and S/P 30 membranes.

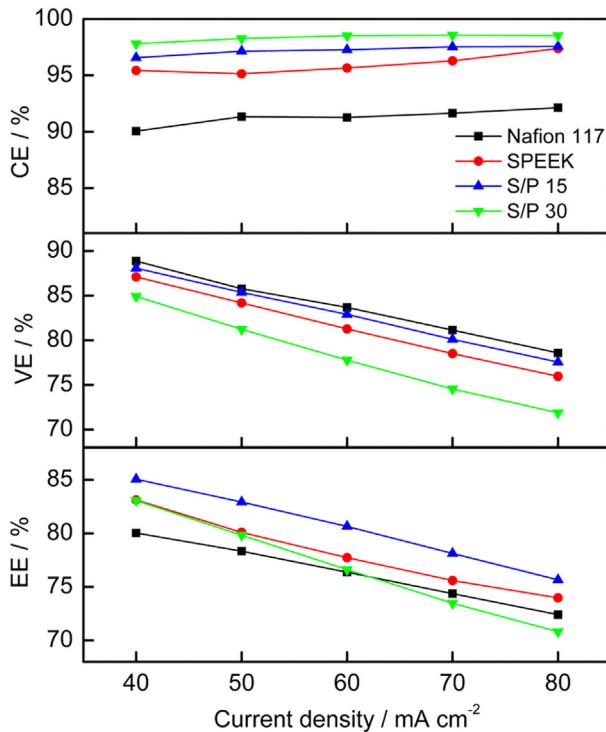


Fig. 9. Efficiencies of VRBs with Nafion 117, SPEEK, S/P 15 and S/P 30 membranes at 40, 50, 60, 70, 80 mA cm^{-2} .

selectivity. The EE of VRB with SPEEK membrane is also higher than Nafion 117 membrane for its higher VO_2^+ permeability. However, the EE of VRB with S/P 30 membrane is lower than Nafion 117 membrane at 70 and 80 mA cm^{-2} , which is due to its higher IR drop caused by lower proton conductivity. Thus, the rank of VE is Nafion 117, S/P 15, SPEEK and S/P 30 membranes for the differences of proton conductivity and ion permeability values.

As the results presented above, the S/P 15 blend membrane has a homogeneous microstructure, suitable physicochemical properties, an excellent ion selectivity, and higher cell efficiencies. In order to evaluate the long lifetime stability of S/P blend membranes, the cycling performances of VRB single cells with S/P 15 and Nafion 117 membrane respectively running at the current density of

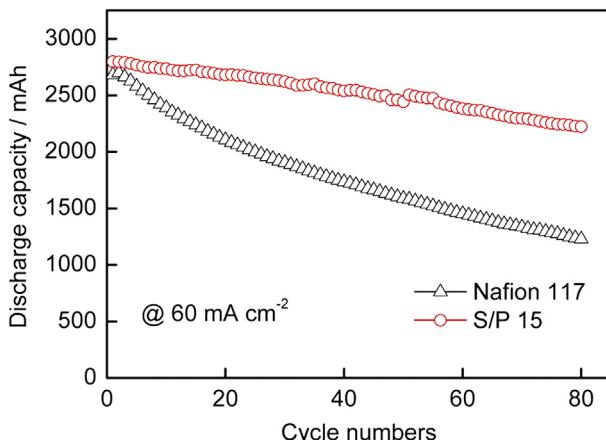


Fig. 10. Cycling performance of discharge capacity declines for VRBs with Nafion 117 and S/P 15 membranes at 60 mA cm^{-2} .

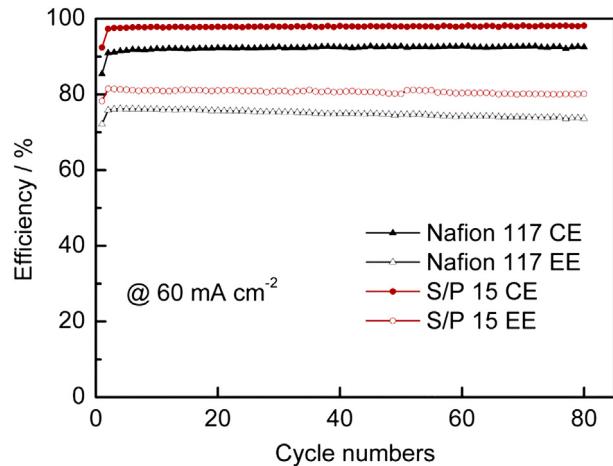


Fig. 11. Cycling performance of efficiencies for VRBs with Nafion 117 and S/P 15 membranes at 60 mA cm^{-2} .

60 mA cm^{-2} are presented in Fig. 10 (discharge capacity decline) and Fig. 11 (CE and EE changes vs. cycle numbers). The discharge capacity decline is caused by the vanadium ions transporting across the membrane. It can be seen that the discharge capacity of S/P 15 membrane is higher than Nafion 117 membrane throughout the cycle life test (Fig. 10), which is due to its lower permeability. Furthermore, the discharge capacity decay rate of VRB with S/P 15 membrane is lower than Nafion 117 membrane. After 80 cycles the discharge capacity of VRB with S/P 15 membrane is 2223 mAh, 79% of the first cycle discharge capacity, which are higher than Nafion 117 membrane (1229 mAh and 46%, respectively). The VRB with S/P 15 membrane shows higher CE and EE (98.0% vs. 92.0% and 81.0% vs. 75.8%, respectively) compared to that with Nafion 117 membrane (Fig. 11), and no obvious CE and EE declines are observed after 80 cycles cell test, which reveals that the structure of S/P 15 membrane is stable.

3.5. Mechanical properties

The mechanical properties of S/P 15 and Nafion 117 membranes are measured and the data are listed in Table 2. The breaking strength and elastic modulus of S/P 15 membrane are larger than Nafion 117 membrane, which indicates that the mechanical properties of S/P 15 membrane are better than Nafion 117 membrane. Furthermore, the percentage elongation of S/P 15 membrane is smaller than Nafion 117 membrane, which is due to the better rigidity of S/P 15 membrane caused by the addition of PVdF. Because of the better mechanical properties, the S/P 15 membrane shows better cycling performance than Nafion 117 membrane as the results presented above. Furthermore, these mechanical properties data are corresponding to the swelling ratio values of these two membranes, indicating that the addition of PVdF indeed improves the swelling behaviors and mechanical properties of blend membranes, which is due to the high hydrophobic nature and high crystallinity of PVdF.

Table 2
Mechanical properties data of S/P 15 and Nafion 117 membranes.

Membrane	Breaking strength (MPa)	Percentage elongation (%)	Elastic modulus (MPa)
S/P 15	41.8	136	433
Nafion 117	19.1	149	189

4. Conclusions

The blend membranes of sulfonated poly(ether ether ketone) (SPEEK) and poly(vinylidene fluoride) (PVdF) are successfully prepared by solution casting method with various mixing mass ratios. The physicochemical properties of various membranes including water uptake, swelling ratio, ion exchange capacity and proton conductivity are characterized, showing that the addition of PVdF indeed limits the swelling behaviors of blend membranes. The VO^{2+} permeability and ion selectivity of blend membranes are improved. The scanning electron microscopy and energy dispersive X-ray spectroscopy results show that the cross-sections of SPEEK/PVdF blend membranes are dense and uniform when PVdF mass ratio ranges from 5 wt.% to 20 wt.%. A blend membrane with 85 wt.% SPEEK and 15 wt.% PVdF (denoted as S/P 15) is chosen for sufficient VRB single cell test. The S/P 15 membrane exhibits longer self-discharge time, higher cell efficiencies (CE and EE), and more stable cycling performance than Nafion 117 membrane. The high performance of S/P 15 membrane is due to its good balance of proton conductivity and ion selectivity, and the stable performance is due to its good mechanical properties and swelling behavior. Therefore, the SPEEK/PVdF blend membrane with excellent performance and low cost is a potential substitute of Nafion membrane for further VRB commercial application.

Acknowledgments

This work was supported by the National Basic Research Program of China (2009CB220105, 2013CB934000), National Natural Science Foundation of China (20973099, 21273129), Shenzhen Science Fund for Distinguished Young Scholars (JC201104210149A) and the Basic Research Program of Shenzhen (JCYJ20120830152316442, JC201005310703A, CXZZ20120614194136123, JC201005310712A).

References

- [1] M. Skyllas-Kazacos, M. Rychcik, R.G. Robins, A.G. Fane, M.A. Green, J. Electrochem. Soc. 133 (1986) 1057–1058.
- [2] M. Skyllas-Kazacos, G. Kazacos, G. Poon, H. Verseema, Int. J. Energy Res. 34 (2010) 182–189.
- [3] A. Parasuraman, T.M. Lim, C. Menictas, M. Skyllas-Kazacos, Electrochim. Acta (2013), <http://dx.doi.org/10.1016/j.electacta.2012.09.067>.
- [4] W. Zhang, J. Xi, Z. Li, H. Zhou, L. Liu, Z. Wu, X. Qiu, Electrochim. Acta 89 (2013) 429–435.
- [5] C. Gao, N. Wang, S. Peng, S. Liu, Y. Lei, X. Liang, S. Zeng, H. Zi, Electrochim. Acta 88 (2013) 193–202.
- [6] A. Di Blasi, O. Di Blasi, N. Briguglio, A.S. Aricò, D. Sebastián, M.J. Lázaro, G. Monforte, V. Antonucci, J. Power Sourc. 227 (2013) 15–23.
- [7] X. Wu, S. Liu, N. Wang, S. Peng, Z. He, Electrochim. Acta 78 (2012) 475–482.
- [8] L. Liu, J. Xi, Z. Wu, W. Zhang, H. Zhou, W. Li, X. Qiu, J. Appl. Electrochem. 42 (2012) 1025–1031.
- [9] L. Liu, J. Xi, Z. Wu, W. Zhang, H. Zhou, W. Li, Y. He, J. Spectrosc. 2013 (2013) 453980.
- [10] X. Li, H. Zhang, Z. Mai, H. Zhang, I. Vankelecom, Energy Environ. Sci. 4 (2011) 1147–1160.
- [11] X. Luo, Z. Lu, J. Xi, Z. Wu, W. Zhu, L. Chen, X. Qiu, J. Phys. Chem. B 109 (2005) 20310–20314.
- [12] J. Xi, Z. Wu, X. Teng, Y. Zhao, L. Chen, X. Qiu, J. Mater. Chem. 18 (2008) 1232–1238.
- [13] N. Wang, S. Peng, H. Wang, Y. Li, S. Liu, Y. Liu, Electrochim. Commun. 17 (2012) 30–33.
- [14] J. Xi, Z. Wu, X. Qiu, L. Chen, J. Power Sourc. 166 (2007) 531–536.
- [15] X. Teng, Y. Zhao, J. Xi, Z. Wu, X. Qiu, L. Chen, J. Power Sourc. 189 (2009) 1240–1246.
- [16] X. Teng, Y. Zhao, J. Xi, Z. Wu, X. Qiu, L. Chen, Acta Chim. Sinica 67 (2009) 471–476.
- [17] X. Teng, Y. Zhao, J. Xi, Z. Wu, X. Qiu, L. Chen, J. Membr. Sci. 341 (2009) 149–154.
- [18] N. Wang, S. Peng, D. Lu, S. Liu, Y. Liu, K. Huang, J. Solid State Electrochem. 16 (2012) 1577–1584.
- [19] X. Teng, C. Sun, J. Dai, H. Liu, J. Su, F. Li, Electrochim. Acta 88 (2013) 725–734.
- [20] Q. Luo, H. Zhang, J. Chen, D. You, C. Sun, Y. Zhang, J. Membr. Sci. 325 (2008) 553–558.
- [21] D. Chen, S. Kim, L. Li, G. Yang, M.A. Hickner, RSC Adv. 2 (2012) 8087–8094.
- [22] D. Chen, M.A. Hickner, S. Wang, J. Pan, M. Xiao, Y. Meng, J. Membr. Sci. 415–416 (2012) 139–144.
- [23] Z. Mai, H. Zhang, X. Li, C. Bi, H. Dai, J. Power Sourc. 196 (2011) 482–487.
- [24] C. Jia, J. Liu, C. Yan, J. Power Sourc. 195 (2010) 4380–4383.
- [25] S. Kim, J. Yan, B. Schwenzel, J. Zhang, L. Li, J. Liu, G. Yang, M.A. Hickner, Electrochim. Commun. 12 (2010) 1650–1653.
- [26] D. Chen, S. Wang, M. Xiao, Y. Meng, Energy Convers. Manage. 51 (2010) 2816–2824.
- [27] S. Xue, G. Yin, Polymer 47 (2006) 5044–5049.
- [28] H. Jung, J. Park, Int. J. Hydrogen Energy 34 (2009) 3915–3921.
- [29] K.A. Sung, W. Kim, K. Oh, M. Choo, K. Nam, J. Park, J. Power Sourc. 196 (2011) 2483–2489.
- [30] H. Jung, J. Park, Electrochim. Acta 52 (2007) 7464–7468.
- [31] J. Woottthikanokkhan, N. Seeponkai, J. Appl. Polymer Sci. 102 (2006) 5941–5947.
- [32] K.D. Kreuer, J. Membr. Sci. 185 (2001) 29–39.